

## PATENT ABSTRACTS OF JAPAN

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### (54) PRODUCTION OF OXIDE CERAMIC

#### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a ceramic material having satisfactory characteristics by uniformly dispersing each metallic element when oxide ceramic is produced by an alkoxide method.

SOLUTION: In a process in which, after a complexing agent having at least one coordination group capable of forming a chelate and at least one polymerizable functional group is coordinate-bonded to a metallic element or its ion in a solvent, the complexing agent is polymerized, a polymer in which the complexing agent is polymerized is produced without bonding the coordination group to the polymerizable functional group or the coordination group to each other and the resultant polymer is made as a precursor.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the oxide ceramic which improved the homogeneity of each metallic element.

[0002]

[Description of the Prior Art]Conventionally, the ball mill method and the sol-gel method are known as a manufacturing method of oxide ceramic.

[0003]The oxide and carbonate of each metallic element are used as a raw material, this raw material is mixed with a ball mill with an insoluble solvent, and the ball mill method dries this, and is a method of obtaining the target oxide ceramic, by carrying out temporary quenching, fabricating after grinding a temporary-quenching thing and carrying out actual calcination further. However, in the ball mill method, when the oxide ceramic made into the purpose was a dielectric, when produced by the ball mill method, the pyrochlore phase which is an unusual appearance was intermingled with the perovskite phase, and there was a problem that dielectric characteristics will deteriorate. Mixture of this unusual appearance has the raw material made of a submicron particle of the oxide of each metallic element.

It originates in the microscopically uneven thing.

As a means for suppressing generation of an unusual appearance, for example in manufacture of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (it outlines the following PMN), to J.Am.Ceram.Soc. and 67[5] p.311 ('84). The method of compounding  $\text{MgNb}_2\text{O}_6$  previously first from  $\text{MgO}$  and  $\text{Nb}_2\text{O}_5$ , and compounding PMN from  $\text{MgNb}_2\text{O}_6$  and  $\text{PbO}$  is indicated. J.Am.Ceram.Soc. and 69 [11] In C287-C288 ('86). The method of compounding  $\text{Pb}_3\text{Nb}_2\text{O}_8$  first from  $\text{PbO}$  and  $\text{Nb}_2\text{O}_5$  and compounding PMN from  $\text{Pb}_3\text{Nb}_2\text{O}_8$  and  $\text{MgO}$  is indicated.

[0004]As a sol-gel method, a metal alkoxide is gelled by hydrolysis and many temporary

quenching and alkoxide processes which carry out actual calcination and obtain an oxide are used in this gel. On the other hand, to USP3,330,697, Nippon Sheet Glass material engineering support community vol.14 (1996), or JP,8-151214,A. A metal complex is made from a metal ion and a complexing agent, a polymer is obtained by making this esterify, and the method of producing ceramics by using this polymer as a precursor is indicated. To J.Am.Ceram.Soc. and 72[8] p.1355 ('89). As a method of compounding PMN,  $\text{Mg}[\text{Nb}(\text{OEt})_6]_2$  is first compounded from  $[\text{Nb}(\text{OEt})_5]_2$  and  $\text{Mg}(\text{OEt})_2$ , The method of obtaining a precursor from  $\text{Mg}[\text{Nb}(\text{OEt})_6]_2$  and  $\text{Pb}(\text{OtBu})_2$  by hydrolysis is indicated.

[0005]

[Problem(s) to be Solved by the Invention]However, in the ball mill method, the shape of a film or fibrous ceramics could not be obtained, and each oxide of the raw material was the floc of the several microns metallic oxide from the submicron, and it was difficult to improve the homogeneity of each metallic element.

[0006]Although the alkoxide process can obtain the shape of a film, or fibrous ceramics by gelling, its metal alkoxide which is a raw material was expensive. When compared with the ball mill method, the homogeneity of each element was high, but in the hydrolysis process, it was difficult for a specific element to improve the homogeneity of each metallic element that it is easy to start ORESHON continuously. On the other hand, although USP3,330,697 and JP,8-151214,A were excellent as a process of the gelling which can obtain a cheap and comparatively uniform ceramics precursor compared with the conventional alkoxide process, there was the following problem. That is, USP3,330,697 uses citrate as a complexing agent. JP,8-151214,A mentions a tetraacetic acid or 5 acetic acid including ethylenediaminetetraacetic acid 2 ammonium as a complexing agent. It is the functional group with same functional group for configurating to the functional group and metal which are used for esterification that it is common in both of the patents. And it is difficult to control the number of the carboxyl groups esterified among two or more carboxyl groups which exist in one complexing agent. In such a case, even if it was the complex stable in the stage of complexing, it was difficult to obtain the number of coordination positions or coordination capability for each complexing agent to have been stabilized in the stage of esterification.

[0007]Then, it aims at obtaining the polymer which this invention solves such a problem and has the stable coordination capability.

[0008]

[Means for Solving the Problem]The above-mentioned purpose is attained by a method of (1) - (7) below.

[0009](1) In a process which polymerizes said complexing agent after carrying out the coordinate bond of a complexing agent with a coordination group in which at least one chelate

formation is possible, and a functional group in which at least one polymerization is possible, and a metallic element or its ion in a solvent, A manufacturing method of oxide ceramic generating a polymer which polymerized said complexing agent without combining said coordination groups and said coordination group, and a functional group in which said polymerization is possible, and making this into a precursor.

[0010](2) A manufacturing method of oxide ceramic of (1) with which said complexing agent is characterized by having a portion in which at least one ionic bond is possible.

[0011](3) A manufacturing method of oxide ceramic given in (1) below 60- $n$  mol% using an organic compound with  $n$  functional groups (however,  $2 \leq n$ ) to said complexing agent in a method of combining between metal complexes, as a linking agent to a coordination part, or (2).

[0012](4) A manufacturing method of oxide ceramic given in (3) combining a coordination part and a linking agent by an ester bond.

[0013](5) A manufacturing method of oxide ceramic given in (3) combining a coordination part and a linking agent by an amide bond.

[0014](6) A manufacturing method of oxide ceramic given in (1) - (5) combining between lapped parts or a lapped part, and a linking agent by addition condensation or copolymerization.

[0015](7) A manufacturing method of oxide ceramic given in (1) - (6) using for a lapped part an organic compound which has an unsaturated bond between at least one carbon-carbon as a complexing agent.

[0016]

[Embodiment of the Invention] This invention is the method of obtaining oxide ceramic, by polymerizing said complexing agent, after carrying out the coordinate bond of a complexing agent, a metallic element, or its ion in solvents, such as water or an organic solvent. The complexing agent used in this invention has a coordination group in which at least one chelate formation is possible, and a functional group in which at least one polymerization is possible.

[0017] Said coordination groups have the structure which is not combined, and the coordination group in which said chelate formation is possible, and the functional group in which said polymerization is possible have the structure which is not combined mutually. Or processing which said coordination groups or said coordination group, and said functional group combine is not performed.

[0018] Thus, by taking the manufacturing method using the complexing agent in which the coordination group for coordination and the functional group for a polymerization are made to exist independently, the influence which polymerization-ization has on a coordinate bond can be improved, and the precursor of oxide ceramic cheaper than a Prior art and uniform can be obtained now.

[0019] Generally the polydentate ligand of a complex is far more stable than a unidentate ligand, and it is known that will originate in the difference of entropy and the direction of a ligand with many coordination groups will serve as a stable chelate complex. The main coordination number of much metal is 4 or more \*\*\*\*s. Two or more \*\*\*\*s of 4 or more \*\*\*\*s of the coordination numbers of the coordination part of these things to a complexing agent are 6 or more \*\*\*\*s still more preferably preferably. When the crack produced in remaining coal or a thin film is taken into consideration as long as there is no trouble in particular since a de binder process is after a polymerization-ized reaction, the lower one of the rate of the organic compound in a polymer is desirable. Therefore, since it can become chelate compound highly if the number of coordination groups increases as it thinks, for example with triethylenetetraminehexaacetic acid (TTHA:10 coordination) etc., it can be said to a de binder process that it is effective.

[0020] As for said complexing agent, it is preferred to have a portion in which at least one ionic bond is possible. This reason is as follows. Generally the complex with an alkaline metal is not stable. So, by having a portion in which an ionic bond is possible, it comes to be able to carry out the ionic bond of said complexing agent with an alkaline metal, and it becomes possible to make it distribute uniformly of it. For example, the hydrogen ion of a carboxyl group (-COOH) is exchangeable for sodium by letting it pass to a sodium hydroxide solution (-COONa).

[0021] In order to make a polymer gel, branched structure is needed for a polymer. However, the polymerization by the functional group of a lapped part is one-dimensional, and since gelling takes place when not taking branched structure, it is expected that two complexing agents may configure in one metal ion at some polymers. However, in order to form clearer branched structure, it is preferred to add a linking agent. However, if a linking agent combines with the coordination group of a coordination part, in order for a coordination group to decrease, it is necessary to minimize the quantity of a linking agent. As for the quantity of a linking agent, below  $60/n$  mol% carries out a linking agent with  $n$  functional groups (however,  $2 \leq n$ ) to said complexing agent. If this range is exceeded, the decrement of a coordination group will become remarkable. As for the quantity of a linking agent, it is more preferred that below  $30/n$  mol% carries out.

[0022] The linking agents in this invention are a complexing agent and an organic compound with two or more combinable functional groups. As a linking agent used preferably, ethylene glycol, glycerin, tartaric acid, 2-aminoethanol, 1,4-butanediamine, 6-aminohexanoic acid, etc. are specifically mentioned. When a linking agent is added, a coordination part and a linking agent are combined by the ester bond, an amide bond, addition condensation, or copolymerization.

[0023] Generally as a donor atom of a coordination group, O, N, S, etc. are used preferably. These donor atoms generally have structures, such as -COO(-) R<sup>3</sup>C-O(-) R<sup>3</sup>C-OH, -NH<sub>2</sub>, and

R<sup>3</sup>C-S (-), in the coordination group of a chelating reagent. So, as for the functional group for a polymerization, it is more preferred that it is an unsaturated bond of carbon-carbon. Since a reaction does not occur when the functional group for a polymerization is an aromatic ring, it cannot use.

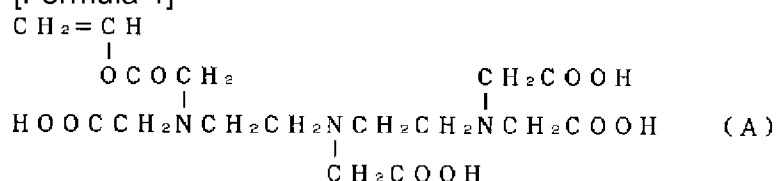
[0024]

[Example] When each metallic element which constitutes oxide ceramic formed a polymer with the manufacturing method of this invention, PMN was compounded as an example which shows that it is distributing uniformly.

[0025] (Example 1) As a complexing agent, what adjusted (A) of a following formula, (B), and (C) so that it might be set to (A)+(B):(C) =9:1 by a mole ratio was used. In the case of this complexing agent, -CH=CH<sub>2</sub> is a lapped part and others serve as a coordination part.

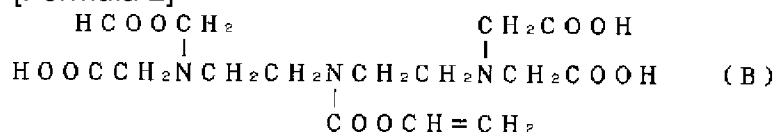
[0026]

[Formula 1]



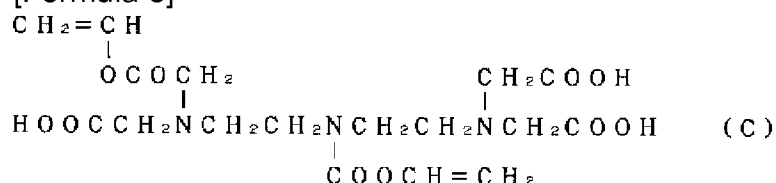
[0027]

[Formula 2]



[0028]

[Formula 3]



[0029] Agitating a complexing agent in a cold nitric acid solution, it added, respectively and Pb (CH<sub>3</sub>OO)<sub>2</sub> and 3H<sub>2</sub>O of the specified quantity, Mg(CH<sub>3</sub>OO)<sub>2</sub> and 4H<sub>2</sub>O, and NbCl<sub>5</sub> were agitated for 10 hours. Each solution was mixed, the ammonia solution was added gradually, and pH was adjusted to six. Then, it added gradually and the ethanol solution of benzoyl peroxide was agitated for 24 hours. Then, after adjusting pH to ten and agitating it for 1 hour, below 10<sup>-3</sup> Torr performed the drying process at 150 °C for 10 hours.

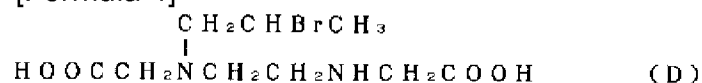
[0030] The de binder of the obtained solid was carried out at 600 °C for 4 hours, actual

calcination was carried out at 800 \*\*, 900 \*\*, and 1000 \*\*, and structure was checked by the powder X diffraction.

[0031](Example 2) As a complexing agent, the thing of the structure of (D) of a following formula and (E) used what was about mixed at a rate of 2:1 by the mole ratio. In the case of this complexing agent,  $-\text{CH}_2\text{CHBrCH}_3$  and  $-\text{CH}(\text{CH}_2\text{Br})\text{CH}_3$  are lapped parts, and others serve as a coordination part. By what is called a dehydrohalogenation reaction, a lapped part serves as an alkene and carries out addition condensation.

[0032]

[Formula 4]



[0033]

[Formula 5]



[0034]Agitating a complexing agent in the cold solution of hydrochloric acid, it added, respectively and  $\text{Pb}(\text{CH}_3\text{OO})_2$  and  $3\text{H}_2\text{O}$  of the specified quantity,  $\text{Mg}(\text{CH}_3\text{OO})_2$  and  $4\text{H}_2\text{O}$ , and  $\text{NbCl}_5$  were agitated for 10 hours. After having mixed each solution, adding the ammonia solution gradually and adjusting pH to seven, reduced pressure drying was carried out, the alcoholic potash was added, and it heated at 80 \*\* for 5 hours. pH was adjusted to seven after ending reaction, it added gradually and the ethanol solution of benzoyl peroxide was agitated for 24 hours. Then, after setting pH to ten and agitating it for 1 hour, below  $10^{-3}$  Torr performed the drying process at 150 \*\* for 10 hours.

[0035]The de binder of the obtained solid was carried out for 600 \*\* 4 hours, actual calcination was carried out at 800 \*\*, 900 \*\*, and 1000 \*\*, and structure was checked by the powder X diffraction.

[0036](Comparative example 1) Following (1) and (2) were produced separately, respectively.

[0037](1) The specified quantity of  $\text{Mg}(\text{OEt})_2$  and  $\text{Nb}(\text{OEt})_5$  was flowed back at 125-135 \*\* among 2-methoxyethanol for 4 hours.

[0038](2)  $\text{Pb}(\text{CH}_3\text{OO})_2$  and  $3\text{H}_2\text{O}$  were dried by heat-treating at 125 \*\* in 2-methoxyethanol.

[0039]Specified quantity mixing of (1) and (2) was carried out, and below after-hydrolysis  $10^{-3}$  Torr performed the drying process at 150 \*\* for 10 hours. The de binder of the obtained solid was carried out for 600 \*\* 4 hours, actual calcination was carried out at 800 \*\*, 900 \*\*, and 1000 \*\*, and structure was checked by the powder X diffraction.

[0040](Comparative example 2) After flowing back the specified quantity of  $\text{Nb}(\text{OEt})_5$  at 110 °C in superfluous ethylene glycol with citrate and 1 hydrate,  $\text{Mg}(\text{CH}_3\text{COO})_2$  and  $4\text{H}_2\text{O}$  of the specified quantity, and  $\text{Pb}(\text{CH}_3\text{COO})_2$  and  $3\text{H}_2\text{O}$  were added, and it agitated for 24 hours.

Then, below  $10^{-3}$  Torr performed the drying process at 150 °C for 10 hours. The de binder of the obtained solid was carried out for 600 °C 4 hours, actual calcination was carried out at 800 °C, 900 °C, and 1000 °C, and structure was checked by the powder X diffraction.

[0041](Comparative example 3) It is made to dissolve in the solution of ethylenediaminetetraacetic acid 2 ammonium with  $\text{Mg}(\text{CH}_3\text{COO})_2$  and  $4\text{H}_2\text{O}$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2$  and  $3\text{H}_2\text{O}$ , and the specified quantity of  $\text{NbCl}_5$ , Superfluous ethylene glycol was added and it was made to react at 130 °C. Ion exchange water was superfluously added to this solution, and the solid was obtained. Filtration recovered after that and below  $10^{-3}$  Torr performed the drying process at 150 °C for 10 hours. 600 °C, the de binder of the obtained solid was carried out for 4 hours, actual calcination was carried out at 800 °C, 900 °C, and 1000 °C, and structure was checked by the powder X diffraction.

[0042]An example as a result of an X diffraction is shown in drawing 1 - 3.

[0043]An X diffraction pattern when it calcinates at 800 °C in Example 1 to drawing 1, an X diffraction pattern when drawing 2 is calcinated at 1000 °C in the comparative example 1, and an X diffraction pattern when drawing 3 is calcinated at 800 °C in the comparative example 2 are shown.

[0044]In Example 1, only the perovskite phase is accepted so that clearly from drawing 1. When it calcinated at 900 °C and 1000 °C in Example 1, the same result was obtained also in Example 2.

[0045]Drawing 2 shows that one peak of pyrochlore exists in 29-30 degrees in 2 theta.

[0046]Drawing 3 shows that two peaks of pyrochlore exist in 29-30 degrees in 2 theta. This peak did not disappear, even when it calcinated at 1000 °C. Even when it calcinated at 1000 °C like the comparative example 2 also in the comparative example 3, in 2 theta, two peaks of pyrochlore existed in 29-30 degrees.

[0047]Since it is difficult to evaluate to think as a cause by which the comparative example 3 became such, it is unknown for details, but in such a reaction path, it is expected that all the carboxyl groups of ethylenediaminetetraacetic acid 2 ammonium have reacted to ethylene glycol. At the time of filtration, magnesium is eluted in a solution, becomes  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{2.97}$  as a result of the X-ray fluorescence of PNM, and is considered that the pyrochlore phase has arisen by it.

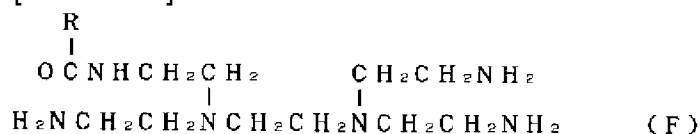
[0048]A carboxyl group is not only like what hydrogen combined but like [ although the above example showed the coordination group or the complexing agent which has only N and COOH



as a donor atom like (A) - (E) ] ammonium salt ( $-\text{COONH}_4$ ). It is not limited, the coupling method of a lapped part and a coordination part is not limited to an ester bond, either, and especially the structure of the coordination part of a complexing agent can use structure as shown in (F) - (I) of a following formula in addition to an example. In (F) - (I), R expresses a lapped part.

[0049]

[Formula 6]



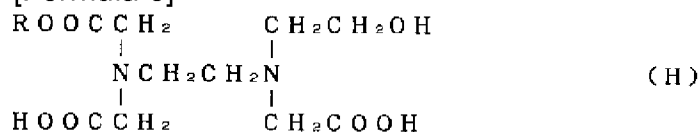
[0050]

[Formula 7]



[0051]

[Formula 8]



[0052]

[Formula 9]



[0053]

[Effect of the Invention] According to this invention, in the manufacturing method of oxide ceramic, the homogeneity of distribution of each metallic element can be improved so that clearly from having stated above. Especially in manufacture of a dielectric, generating of the unusual appearance resulting from the unevenness of distribution can be suppressed, and dielectric ceramic with the good characteristic can be obtained.

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[Translation done.]